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OF THREE POLYSILOXANE GUMS

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ABSTRACT

Because of the termination of both silicone gums and cellular silicone products by Union Carbide Corporation, it has been necessary to evaluate commercial alternatives as well as potential developmental polymer replacements for W97. For this reason, LLNL, Bendix Corporation, and the Pantex plant have undertaken the development of characterization methodology for silicone gums as well as the concomitant chemical and physical analyses of the polysiloxanes RG97, SE54 and Y3976. The most viable test battery to arise from this study is the determination of $\bar{M}_w$, $\bar{M}_n$, and MWD by GPC, vinyl and phenyl contents of the gums by magnetic resonance or chromatographic techniques, and volatile content of the gums by thermogravimetric analysis. A comparison of the siloxane gums indicates that the random SE54 is a high phenyl content, high molecular weight, low volatile resin of high quality. RG97 is in contrast a relatively low molecular weight, high volatile content gum that is inferior to SE54. The developmental material Y3976 which is synthesized by a different procedure, is close in properties to the SE54 gum but is somewhat lower in phenyl content.

INTRODUCTION

Cellular silicone cushions of varying densities, shapes and genesis have been integral members of Lawrence Livermore National Laboratory (LLNL) weapon systems for many years. Cushion materials, filled molding compounds and base polysiloxane resins were supplied to the Department of Energy (DOE) by Union Carbide Corporation (UCC) for a long period of time until these materials were withdrawn sequentially from the open marketplace in the middle 1970's. Initially, when cellular silicone supply was terminated owing to limited commercial demand, UCC agreed to supply the base silicone gum W97 and processing plans to Bendix Corporation-Kansas City Division (BKC) for DOE production of cellular silicone. Shortly thereafter, W97 gum was also withdrawn from production and the DOE complex was left in a vulnerable position with only two alternatives: 1) find a commercially available gum stock as the base resin for cellular materials; or 2) synthesize our own polysiloxanes to be used as the base resin.

Alternative 2) has met with success in both the synthesis of polysiloxane gums at LLNL. Because of programmatic time constraints it has been necessary to analyze and characterize any commercially available resin systems which might prove to be feasible substitutes for UCC's W97.

The gums characterized include Rhodia Corporation's RG97, General Electric's SE54, and UCC's Y3976. Y3976 is a development block copolymer which never was commercially available. RG97 and SE54 are random terpolymers of cyclic tetrasiloxanes which contain the diphenyl-, dimethyl-, and methylvinylsiloxane subunits randomly arranged along the polymer backbone. Y3976 contains identical subunits but with a much greater degree of regularity induced by the block copolymer arrangement.

While there is an ongoing and continuous effort in testing of the cellular cushions that have been formulated from these silicone gums, very little coordinated work has been accomplished on testing of the silicone gums themselves. In April of 1979 representatives of the Polymeric Materials group

at LLNL and the Materials Engineering group of BKC met in Kansas City and
formulated a coordinated plan of attack to characterize these gums. A testing
matrix for the agencies involved (LLNL, BKC, and Mason & Hanger-Silas Mason
Pantex plant (PX)) was agreed upon. The key Pantex personnel, while not
present at this initial meeting, agreed later to implement the test matrix in
full. The initial testing and methods agreed upon, and respective agencies
are indicated in Table 1.

All phases of this project have been completed and this report details the
results using the various test methods. Bendix and Pantex results will be
discussed in less depth than the LLNL results. The aim of this test matrix
was to establish a methodology for determining the chemical and structural
composition of the gums so that, in the future, incoming polymers would be
characterizable and the composition comparable to other silicones. On this
basis, the suitability of base gums for compounding into cushions could be
established or disproved.

TABLE 1

ANALYSIS	AGENCY	METHOD
Molecular Weight $\bar{M}_w$, $\bar{M}_n$, MWD	BKC	Gel Permeation Chromatography (GPC), light scattering spectrometry
	LLNL	GPC
	PX	GPC
Vinyl Content (as $-CH=CH_2$)	BKC	Gas Chromatograph (GC)
	LLNL	Fourier Transform Nuclear Magnetic Resonance (FTNMR)
	PX	FTNMR and IC titration
Phenyl Content (as $-C_6H_5$)	BKC	GC
	LLNL	FTNMR
	PX	FTNMR
SiOH	BKC	Infrared (IR)
	PX	Manometry

Table 1 continued

ANALYSIS	AGENCY	METHOD
Volatiles Content	BKC	GC
	LLNL	Weight Loss, Thermogravimetric Analysis (TGA)
Elements K, P, N	BKC	Selected Methods
	LLNL	Selected Methods
Dynamic Viscosity	BKC	Oscillatory Cone and Plate
	LLNL	Oscillatory Cone and Plate

MATERIALS

The gums tested, RG97 (lot 17), SE54 (lot 161) and Y3976 (lot 11811) were blended at BKC and shipped to Pantex (PX) and LLNL in June of 1979. RG97 and SE54 were recent acquisitions and as such were relatively "fresh." The condensation polymer Y3976 was procured by LLNL from Union Carbide several years ago and a representative sample was extracted from the remaining material. The materials were blended at BKC by Dr. G. Keith Baker to assure uniform specimens. This was accomplished by selecting specimens of gum from different places in the lot of choice. Identical specimens were then sent to each of the other two agencies with one sample retained by BKC.

The choice of these three gums as test samples was mandated by the fact that the RG97 and SE54 materials are currently the only commercially available silicone gums in the United States suitable for conversion to cellular silicone cushions; Y3976 was the only polysiloxane block copolymer available for testing at the time of initiation of the program.

LLNL RESULTS

Molecular Weight: $\bar{M}_w$, $\bar{M}_n$, MWD

Jack Clarkson of the General Chemistry Division at LLNL tested these
gums. They are reported in Table 2 as polystyrene equivalents and were run in
THF solutions. The confidence level for each reported number is 95 percent.

TABLE 2

	RG97	SE54	Y3976
C (mg/50ml solution)	204.0	201.0	208.5
$\bar{M}_n$	228200 ± 7280	380800 ± 4830	314900 ± 7000
$\bar{M}_w$	577600 ± 14000	863570 ± 14050	799100 ± 13200
MWD	2.53 ± 0.06	2.25 ± 0.06	2.54 ± 0.05

Molecular weights were also determined by least squares fitting of
intrinsic viscosity measurements made on the gums. The results are presented
in Table 3.

TABLE 3

GUM	Det'n 1	Det'n 2	Det'n 3	$\underline{MW}_{ave}$
RG97	518000	520000	587000	542000 ± 40000
SE54	840000	839000	797000	825000 ± 20000
Y3976	658000	706000	665000	676000 ± 20000

Vinyl and Phenyl Content

Relative vinyl and phenyl contents in the three gums were determined by
continuous wave proton nuclear magnetic resonance spectroscopy (pmr). The

measurements were not made utilizing Fourier transform techniques as indicated in Table 1. They were generated by summing repeated continuous wave scans at a frequency of 60 megaHertz. Jim Happe of the General Chemistry Division performed the analyses. The results are presented in Table 4.

TABLE 4

Sample	% Methyl (CH_3)*	% Phenyl (C_6H_5)	% Vinyl $(CH = CH_2)$*
Y3976	31.8 ± 4.5	7.78	0.087 ± 0.003
SE54	35.8 ± 1.75	11.98	0.066 ± 0.003
RG97	35.3 ± 0.75	9.80	0.075 ± 0.002

*Uncertainties are the average deviation from the mean of three or four determinations. Relative percentages are normalized to one phenyl group.

Volatiles Content

The volatiles contents of each of the three gums were determined by two different techniques - weight loss after heat treatment and thermogravimetric analysis (TGA) which records weight loss as a function of temperature. The results of these measurements are presented in Table 5.

TABLE 5

	RG97	SE54	Y3976
Volatiles by weight loss	6.2 $(\delta = .3)$	2.1 $(\delta = .2)$	2.6 $(\delta = .2)$
Volatiles by TGA	7.5	5.8	5.2
Event onset (^oC)	RT	90	60
Event peak (^oC)	--	200	210
Event end (^oC)	240	300	320
T_g (by DSC) (^oC)	-112	-108	-114

RG97 has the highest volatiles content of the three gums. The relative ordering of SE54 and Y3976 is reversed depending upon the method used.

Elemental Analysis for Potassium, Phosphorus, and Nitrogen

Elemental analysis for potassium and phosphorus were run by Bob Lim and for nitrogen by Lew Gregory, both of the General Chemistry Division. The primary reason for the determination of the K, P, and N content of these gums is to ascertain catalyst type employed in polymerization, i.e., potassium, tetramethylammonium or tetrabutylphosphonium silanolate. Analysis results are presented in Table 6.

TABLE 6

Gum		K(ppm)	P(ppm)	N(ppm)
RG97	(1)	45.0	17	none detectable
	(2)	45.2	<10	---
	(3)	44.0	<10	---
SE54	(1)	15.7	<10	none detectable
	(2)	15.1	<19	---
	(3)	14.2	<10	---
Y3976	(1)	0.58	<10	none detectable
	(2)	0.69	<10	---
	(3)	0.72	<10	---

It appears from these results that both RG97 and SE54 were polymerized through initiation with a potassium silanolate (K-catalyst) initiator. Based only on these results it would be impossible to confidently say which catalyst was employed to prepare the prepolymer Y3897 used in the preparation of Y3976. From previous information,[1] however, we are aware that a tetramethylammionum silanolate (N-catalyst) was used to prepare this oligomer.

Dynamic Viscosity

Dynamic viscosities of the three polymers were determined on a Rheo-
metrics Mechanical Spectrometer (RMS). Storage and loss moduli (G' and G"
respectively) and dynamic viscosity (N' or G"/ω) were determined as a
function of the oscillatory frequency (ω in radians/second). Plots of the
logs of G', G", and N' as a function of log frequency are illustrated in
Figure 1 (RG97), Figure 2 (SE54), and Figure 3 (Y3976). The data are
available in tabular form to interested parties. Perhaps the only
definitive statement that can be presently made on the basis of dynamic
viscosities measured here is that the gums are viscoelastically
distinguishable. Not surprisingly, the storage modulus and dynamic
viscosity of the gums vary directly with molecular weight.

BENDIX TEST RESULTS

The Bendix results were assembled and coordinated by Dr. G. Keith
Baker and are listed in Table 7.

TABLE 7

SUMMARY OF BENDIX ANALYSES AND CHARACTERIZATION OF SILICONE GUMS SE54, RG97, and Y3976

	Y3976	RG97	SE54
$\bar{M}_w$, light scattering	1,335,000 $\pm$ 54,000	924,000 $\pm$ 35,000	1,716,000 $\pm$ 12,000
$\bar{M}_w$, GPC	463,000 $\pm$ 9,400	391,000 $\pm$ 7,300	465,000 $\pm$ 7,700
$\bar{M}_n$, GPC	125,800 $\pm$ 6,205	121,500 $\pm$ 3,300	79,000 $\pm$ 3,100
MWD, GPC	3.68	3.22	6.28

Table 7 continued

	Y3976	RG97	SE54
SiOH	ND	ND	ND
% N	.01	ND	.01
% Vinyl, GC	0.067 ± .001	0.081 ± .002	.069 ± .002
% Phenyl, GC	7.31 ± .52	9.41 ± .25	11.75 ± .25
% Phenyl, IR	12.90	15.33	15.27
% Volatiles, GC @ 300°C	17.6	57.2	12.9
% Volatiles, GC @ 150°C for 16 hours	4.57 ± .19	9.46 ± .16	5.06 ± .13
K, ppm	.44 ± .16	27.4 ± 1.1	8.2 + 1.7
P, ppm	4.7	0.1	0.1

Dr. Baker, in conjunction with Eric Grotheer of BKC has published an excellent report on the characterization of all the components of cellular silicone materials.[2] Among these are six silicone gums, SE54 and RG97 included. The results on these two materials appear to be consistent with the results obtained here in the Round Robin test series. All instrumental and chemical methods and techniques are explained in reference 2. The only deviation here from the agreed-upon test matrix is the inclusion of analyses for phenyl content in the gum by infrared monitoring of the phenyl absorbance.

PANTEX TEST RESULTS

The interest of the Pantex organization in silicones for cellular materials is not as intense as that at BKC and LLNL although there has been an extensive effort in all phases of formulation and application of silicone potting compounds. Dr. Gary L. Flowers of the Pantex Development Division kindly agreed to implement and coordinate a polysiloxane test series at Pantex. The results of that parallel effort are included in Table 8.

TABLE 8

SUMMARY OF PANTEX ANALYSIS AND CHARACTERIZATION OF SILICONE GUMS SE54, RG97, and Y3976

	Y3976	RG97	SE54
$\bar{M}_w$, GPC	736,000	524,000	762,000
$\bar{M}_n$, GPC	196,000	147,000	247,500
MWD, GPC	3.8	3.6	3.1
% SiOH (as hydroxyl by reaction with $LiAlH_4$)	0.504 ± 0.002	0.630 ± 0.12	0.252 ± 0.03
% Vinyl (ICl)	1.093 ± 0.009	1.137 ± 0.002	1.320 ± 0.017
% Phenyl, Standard	7.9 ± 0.45	10.7 ± 1.10	13.2 ± 0.042
% Phenyl, Vacuum Dried	7.0 ± 0.17	9.2 ± 0.06	11.2 ± 0.15

It should be pointed out here that the Pantex test for hydroxyl groups does not distinguish silanol units from any other hydroxyl unit. Thus any residual moisture in the gum or xylene solvent contributes to the total hydroxyl content. For this reason, it was decided that in the future, silanol content would not be determined by measurement of hydrogen generated after $LiAlH_4$ reaction with polysiloxanes in xylene solution.

DISCUSSION AND CONCLUSIONS

There are several conclusions which may be drawn based on the results of the three agencies involved. Let us first review the compositional nature of these polymers. By compositional, we are referring to the organic moieties (CH_3, C_6H_5, $CH=CH_2$) present and the endcapping of the polysiloxanes (silanol content). Three methods were used to determine vinyl content: nmr, gas chromatography and reaction with iodine monochloride. These percentages of vinyl are compared in Table 9.

TABLE 9

SUMMARY OF VINYL CONTENTS (As $CH=CH_2$ %)

TECHNIQUE	RG97	SE54	Y3976
ICl	1.137	1.320	1.093
GC	0.081	0.069	0.067
CW nmr	0.075	0.066	0.087

The ICl titration technique yields very high contents of vinyl. This is most likely due to nondiscriminatory attack upon phenyl unsaturation as well as upon vinyl as Lim has demonstrated.[3] These materials nominally have vinyl contents of 0.063 to 0.094 percent (as $CH=CH_2$) and the values obtained by either chromatographic or magnetic resonance are comparable. All of these silicone gums have vinyl contents within the limits previously established as preferable. The ICl technique should be abandoned.

Phenyl content of these three base polymers should fall in the range of 7.01 to 11.67 percent (as C_6H_5). Phenyl content was determined by proton nmr, gas chromatography, quantitative infrared technique and proton Fourier Transform nmr (FTnmr). The results are compared and contrasted in Table 10.

TABLE 10

SUMMARY OF PHENYL CONTENTS (As C_6H_5)

TECHNIQUE	RG97	SE54	Y3976
GC	9.41	11.75	7.31
IR	15.33	15.27	12.90
Proton nmr	9.80	11.98	7.78
Proton FTnmr	10.7	13.2	7.9
Proton FTnmr (vacuum-dried)	9.2	11.20	7.0

The infrared technique affords considerably higher phenyl content values than the remaining techniques. Vacuum drying of the gums for FTnmr studies appeared to reduce the apparent phenyl contents. These vacuum-dried samples then yielded values which are very comparable to those values obtained by CWnmr and GC. Any of these three techniques appear to offer reliable values for phenyl content.

Concerning the materials themselves, SE54 appears to be the most phenyl-rich polymer with Y3976 having the lowest comparative phenyl content. As a first approximation, one would expect SE54 to be the stiffest, highest modulus material with Y3976 the "softest." These two materials bracket RG97 in phenyl content. Obviously, methyl contents can be determined differentially by a knowledge of the vinyl and phenyl contents.

It was mentioned earlier that silanol as determined by reaction in xylene with $LiAlH_4$ is an unsatisfactory, nondiscriminatory technique. Quantitative infrared analysis of these gums at BKC yielded no determinable SiOH. The Bendix-devised test should be of greater import in Y3976-like materials which are produced by a condensation polymerization of amine- and silanol-terminated prepolymers. The presence of unreacted silanol is more probable in this system. This will be an important analytical technique should condensation, block polysiloxanes become base materials for future cushions.

Volatiles were determined by weight loss, TGA and gas chromatographic techniques (at 300°C and at 150°C held for 16 hours). Because of the method of preparation, RG97 and SE54 are expected to have some unreacted cyclic tetrasiloxanes as well as low molecular weight oligomers. On the other hand, because of the condensation polymerization employed to synthesize Y3976, little volatile content is expected for the condensation polymer. One would predict on this basis, and predicated on General Electric's marketing of SE54 as a devolatilized gum, that the ordering on the basis of increasing volatiles should be Y3976 < SE54 < RG97. By TGA and GC at 150°C this is indeed the ordering we find. For the weight loss technique SE54 and Y3976 have a

reversed order. For GC at 300°C this is also true. This last technique is of questionable value because, at the high temperature employed, chain scission is probably occurring. This accounts for the high volatiles contents found (57.2, 17.6, and 12.9 for RG97, Y3976, and SE54 respectively). The numerical values for TGA and GC at 150°C are comparable in magnitude and ordering. Either technique is of utility here. The gums SE54 and Y3976 are definitely superior to RG97 in terms of the level of residual volatiles.

The chemical analyses for potassium, phosphorous and nitrogen were undertaken to ascertain the type of initiator used to commence polymerization. From the relatively high levels of potassium found by LLNL and BKC it appears that potassium silanolate was used to initiate reaction in SE54 and RG97. Nitrogen was undetected by LLNL and was found to be only 0.01 percent for SE54 by BKC. While there are low levels of phosphorous in all three materials, this is not indicative of the use of tetrabutyl-phosphonium silanolate as the catalyst.

Each of the three agencies determined weight average ($\overline{M}_w$) and number average ($\overline{M}_n$) molecular weights and polydispersity (MWD). These fall in the order SE54 > Y3976 > RG97 for $\overline{M}_w$ and $\overline{M}_n$. All agencies used polystyrene equivalents and tetrahydrofuran solutions. The polydispersities as determined by LLNL were consistently less than those obtained by BKC or PX. The differences in magnitude of $\overline{M}_w$ and $\overline{M}_n$ among the three agencies are explicable in terms of the differences in instrumentation, techniques, and personnel involved in testing. LLNL and PX are comparable numerically while the BKC-generated weights are consistently lower by GPC. It is interesting to note that the ordering of gum weights as determined by light scattering spectrophotometry (BKC) and intrinsic viscosity (LLNL) is identical to the ordering established earlier by GPC studies at each site. SE54 appears to be a relatively high molecular weight random polysiloxane with RG97 being lower in molecular weight. Y3976 falls between the two extremes.

For the study of dynamic viscosities, as mentioned earlier, there appears to be a rough linear correlation between storage modulus or dynamic viscosity of the gums and gum $\overline{M}_w$. While the results are not illustrated here, BKC has indicated similar results from their study of dynamic viscosities of the three polysiloxanes.[2]

SUMMATION

As mentioned in the introduction, our goal in undertaking this project was principally to establish a methodology for analyzing polysiloxanes that could be refined to the point where it may be used on a day-to-day basis to accept or reject incoming base gums. Toward this goal we have been successful. We believe that a standard series of tests to be run on polysiloxanes arriving at BKC for conversion into cellular silicone cushions should be:

1. Determination of $\bar{M}_w$, $\bar{M}_n$, and MWD by gel permeation chromatography.

2. Vinyl content by CWnmr or GC.

3. Phenyl content by CWnmr, FTnmr or GC.

4. Volatiles content by TGA or GC (at 150°C for 16 hours).

An additional analysis which was not included here but which will probably prove useful in the long run is analysis of moisture so that residual H_2O levels can be established.

The remaining tests that were mentioned here help establish the nature of the polymers but should not be run routinely. In consideration of all these tests, certain conclusions on the gums may be made. Of the two commercial gums examined, SE54 is a high $\bar{M}_w$, low volatile material with a phenyl content that is somewhat high. These characteristics yield a somewhat stiff, high modulus material. RG97 has an intermediate phenyl content but is high in volatiles content and somewhat low in $\bar{M}_w$. This produces a soft, less creep-resistant material with a high level of internal contaminants. Y3976, which was prepared by an entirely different synthetic procedure, is closer in character to SE54 than to RG97: low volatiles and high $\bar{M}_w$ but a low phenyl content. These factors produce a gum of intermediate stiffness and good purity. When the entire test matrix and all of the gum properties are considered, it may be stated that none of the three candidate materials has eliminated itself chemically. Further testing of the intermediate compounding stages and final cushions are

necessary to eliminate any of the materials. Setting stringent limits on
the chemical and physical properties of incoming gums based on the
recommended test battery will be another way of eliminating unsuitable
polysiloxanes early.

ACKNOWLEDGEMENTS

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2.   G. K. Baker and E. W. Grotheer, "Polymer-Chemical Characterization of
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3.   Robert Lim, "The Determination of Vinyl Groups and Active Hydrogen in a
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Fig. 1. Dynamic viscosity of Rhodia RG97.
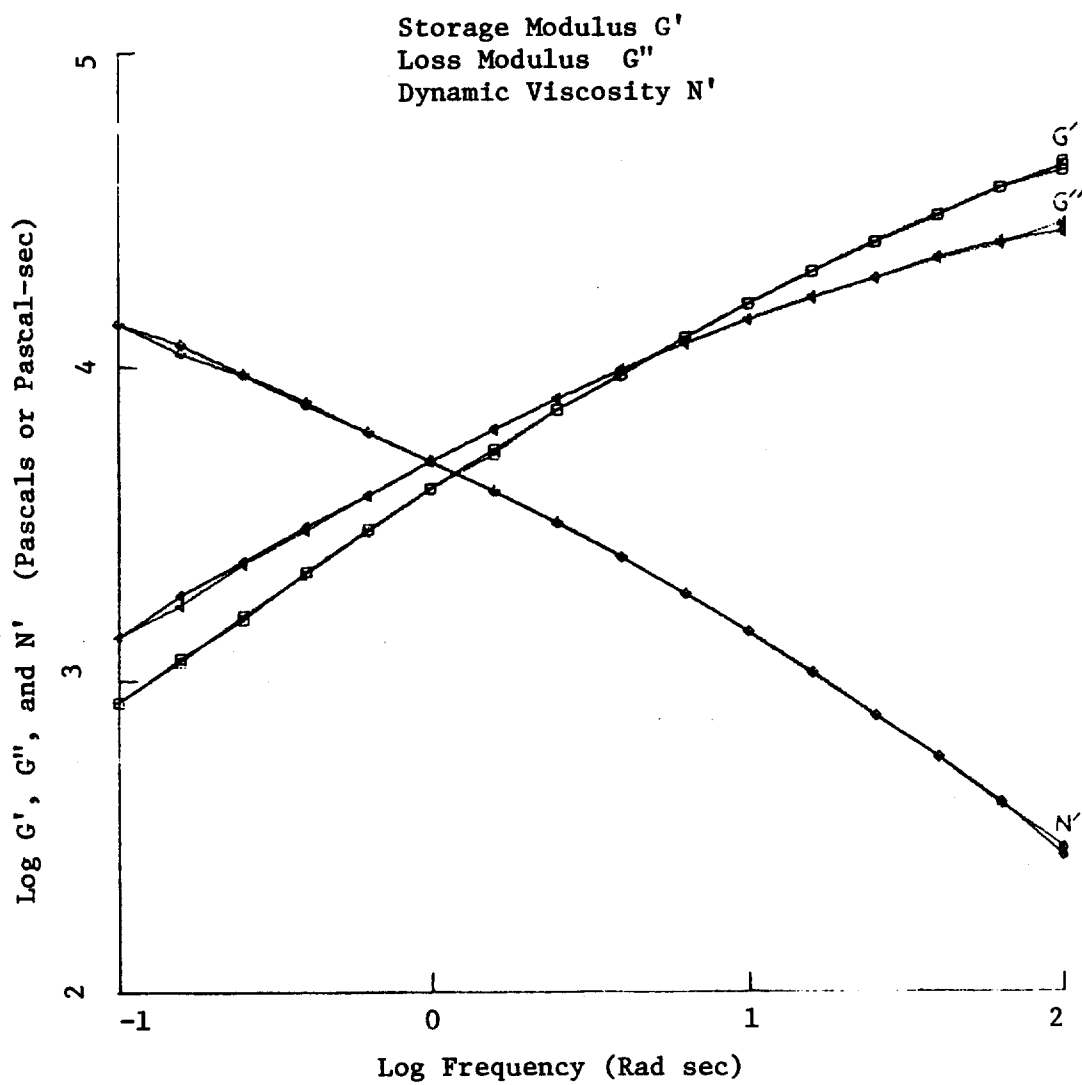
Storage Modulus G'
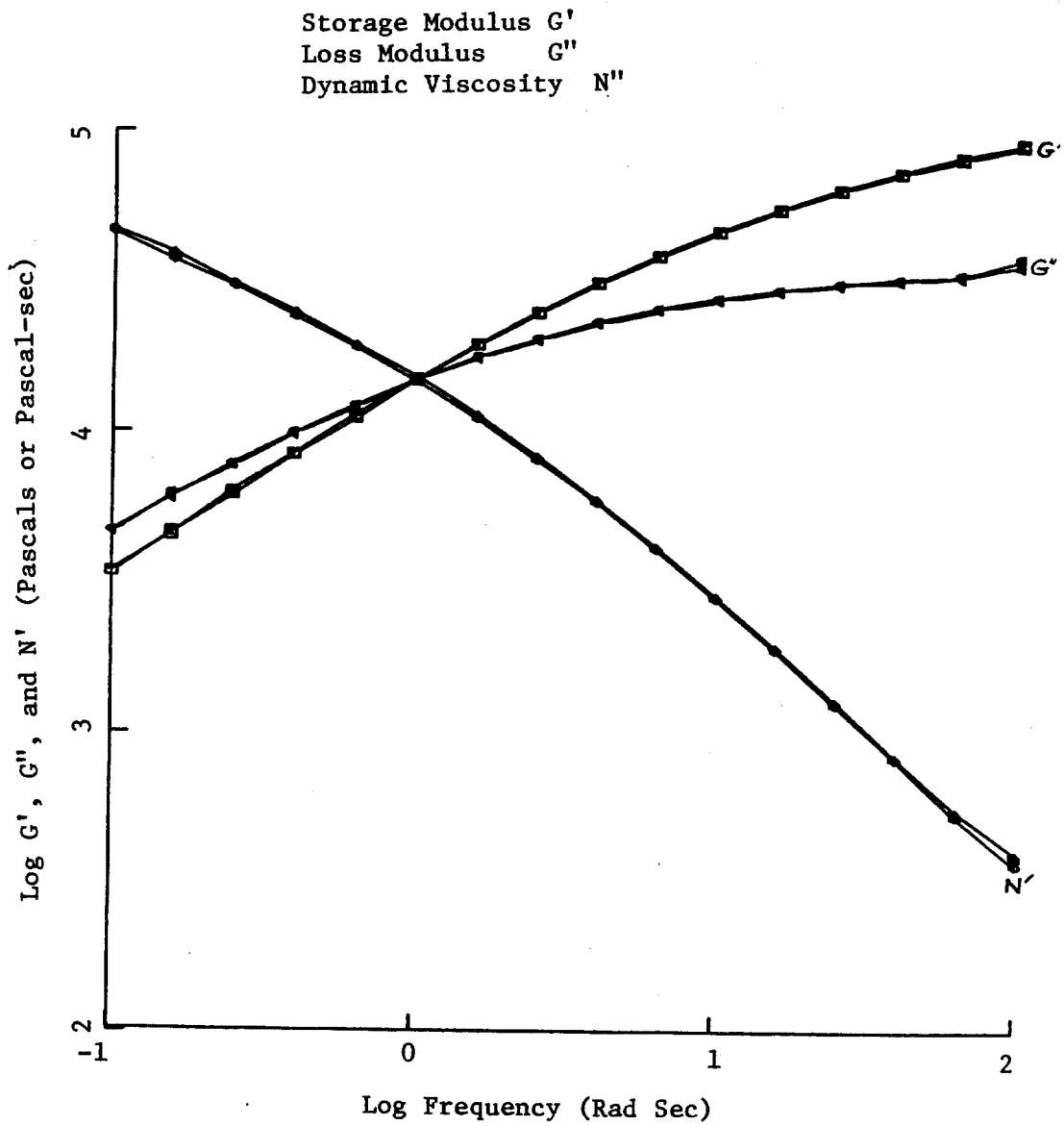Loss Modulus   G"
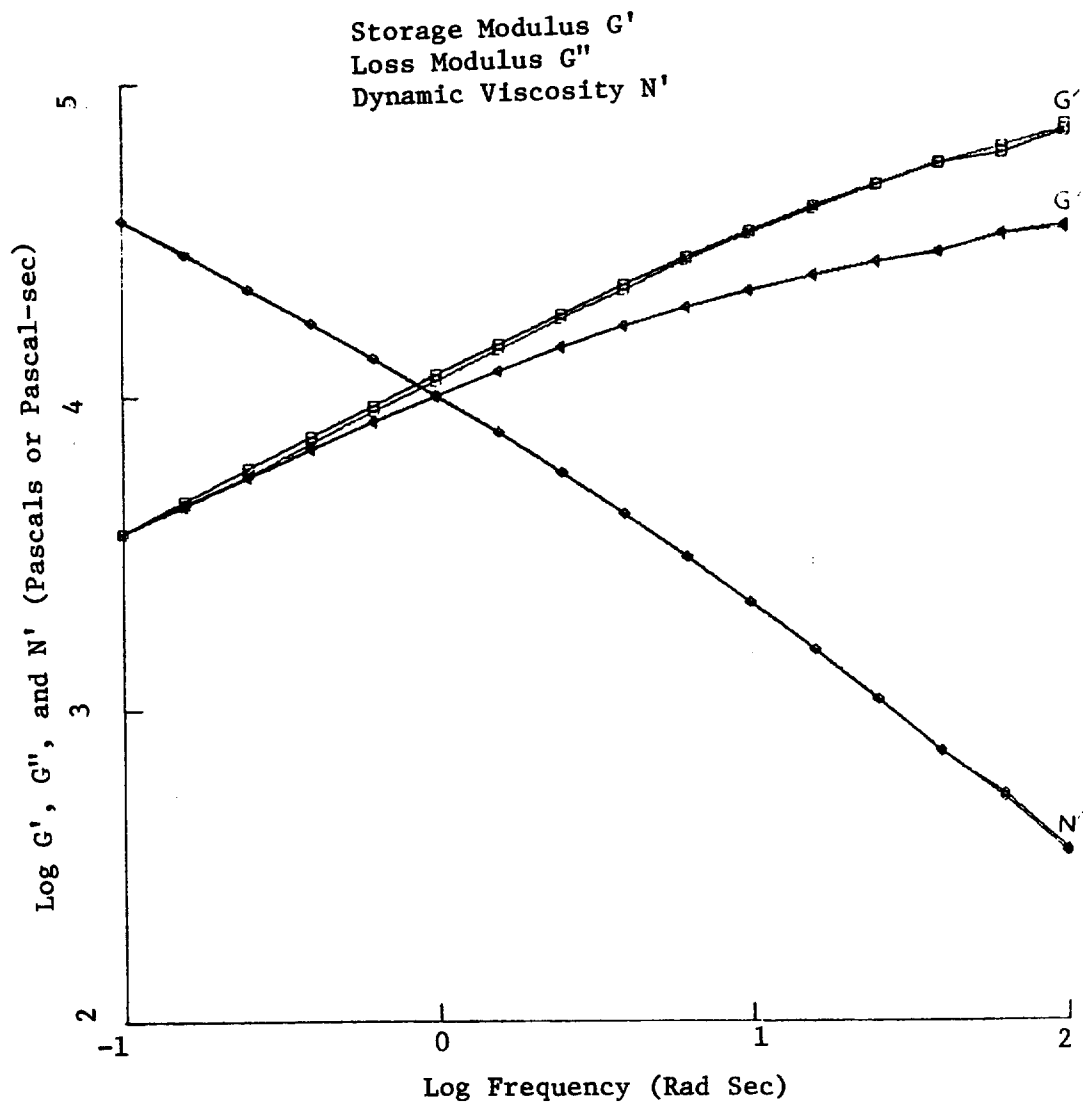Dynamic Viscosity N"

Fig. 2. Dynamic viscosity of GE silicone Gum SE54.

Fig. 3. Dynamic viscosity of Union Carbide Y3976.